

Supported Electrolyte Thin Film Synthesis of Solid Oxide Fuel Cells

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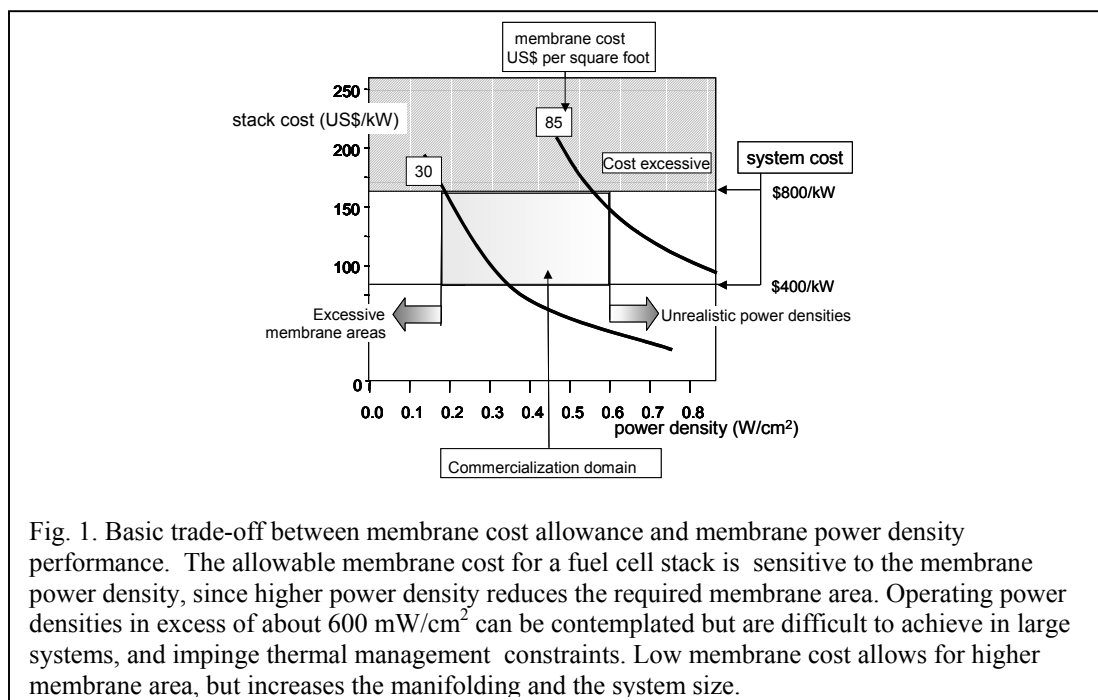
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Introduction:

Solid oxide fuel cells rely on oxygen ion or proton conduction through ceramic electrolytes. The transport rates of oxygen ions of bare protons of known electrolytes is, however, presently too low to allow for practical devices at temperatures much below 500°C. This lower temperature limit is determined not only by the conductivity of the electrolyte, but also by electrode performance and by the advantage of the ability to extract additional energy from the fuel cell exhaust gases. Temperatures above 800°C lead to rapid electrode reactions and exhaust gases that may be used in turbine bottoming cycles. Unfortunately, such temperatures severely restrict the materials that are compatible and can resist the operating conditions for long times. While high temperature systems (*i.e.* above 950°C) have demonstrated extended performance, their economically viability remains a persistent concern.

The cost challenge that fuel cells must meet can be simply illustrated when the usual assumption is adopted that the fuel cell stack should constitute no more than 1/5 of the system cost. Economic competitiveness has been suggested at a system cost with an upper limit of \$800/kW and a stretch limit of \$400/kW. Fig. 1 incorporates this assumption indicating that the stack membrane cost should be approximately between 80 and 165\$/kW. This does not leave much for processing, and could eliminate a number of otherwise promising processing approaches.

Reducing the temperature of operation to below 800°C and, preferably, even lower greatly extends the choice of compatible materials. The reduced temperatures require the use of thin solid electrolytes, typically less than 25 µm thick, to reduce the ionic resistance of the electrolyte. Such electrolytes are not sufficiently robust by themselves, and must therefore be produced on either the anode or cathode of the fuel cell, where this electrode now also has a mechanical support function in addition to all its electrical functions. The production of supported thin film solid oxide electrolytes on a porous support electrode in an economically viable manner is therefore one of the essential aspects of reduced temperature thin film solid oxide fuel cells. The fabrication process itself subjects the materials to conditions that differ significantly from those of the fuel cell operating environment, and significant challenges can be encountered in assuring that promising materials combinations survive the processing steps.



The vast majority of the thin film solid oxide fuel cells use yttria stabilized zirconia (YSZ) as an electrolyte. This material has been extensively examined and has the advantage of high stability and compatibility with the broadest range of electrode materials. In thin film form it is suitable down to approximately 650°C. For lower temperatures, alternative electrolytes, with higher oxygen ion conductivity can be considered (*e.g.* Ceria -based ones) although many of these introduce new difficulties, such as higher reactivity, electronic conductivity, or thermal expansion mismatch. In this chapter we describe several of processing methods that can lead to the formation of thin, dense ceramic electrolytes on porous support electrodes. Only a very limited number of these can be reasonably projected to be sufficiently simple to allow for economic exploitation.

SOFC membrane architectures.

Presently, the most widely examined thin film SOFC is anode supported, whereby the anode consists of a YSZ–Ni cermet. This electrode is compatible with processing temperatures in excess of 1400°C with YSZ electrolytes, allowing significant processing flexibility. Alternative anode support structures involve the use of ferritic steels, or conductive oxides such as SrTiO₃ derivatives¹. SrTiO₃-based anodes appear to promise

¹ D. P. Fagg, V. V. Kharton, A. V. Kovalevsky, A. P. Viskup, E. N. Naumovich, and J. R. Frade, *J. European Ceramic Soc.*, **21**, 1831(2001).
O. A. Marina, N. L. Canfield and J. W. Stevenson, *Solid State Ionics*, **149**, 21(2002).

interesting performance, but at this time are less well studied. The use of ferritic steels, either chromia formers or alumina formers restrict the environment of the fabrication process to reducing atmospheres and temperatures below 1300°C.

Lanthanum strontium manganate (LSM) cathode supported thin film electrolytes have been used with considerable success in the Siemens Westinghouse Power Generation tubular design². For the popular LSM cathode and their derivatives, processing temperatures should remain below about 1350°C to avoid the formation of resistive lanthanum zirconate interfaces. Interface impedances can be detrimental, and their effect is more pronounced the lower the cell operating temperatures. In spite of the proven success of the cathode-supported architecture, current developments continue to focus on the Ni-YSZ anode supported YSZ electrolytes, which may offer advantages in reaching high power densities with thin LSM cathodes.

Processing Methods

Almost all known processing techniques have been tried for producing thin electrolyte films on porous support electrodes. The majority of these can be suitable for laboratory demonstration, but would find adoption in a mass production environment difficult or cost prohibitive.

Vapor phase methods

The vapor phase methods employ volatile mixtures of the compounds that constitute the electrolyte. Such compounds are typically chlorides or volatile metallorganics that are reacted with water vapor or oxygen, to deposit the oxide on the heated substrate. Growth rates of the films are typically less than 10 µm/hr. The films are produced on one substrate at the time, posing some potential difficulties for mass production. The required substrate temperatures vary widely, with the best results obtained at temperatures in excess of 500° C. Lower temperatures tend to promote nucleation in the gas phase, and deposition rates dominated by surface reaction rates. This can lead to deposited films with compositions different from that of the feed gas. At higher temperatures mass transport in the gas phase limits the deposition rate, yielding deposited films with compositions close to that of the feed gas. These issues were discussed recently in some detail by Akiyama et al³ for low pressure YSZ deposition from metalloorganic zirconia and yttria compounds.

² S.C. Singhal, "Advances in solid oxide fuel cell technology", *Solid State Ionics*, **135**, 305(2000).

³ Yasunobu Akiyama, Nobuyuki Imaishi, Young-Sik Shin, Sang-Chul Jung, Macro- and micro-scale simulation of growth rate and composition in MOCVD of yttria-stabilized zirconia, *Journal of Crystal Growth* 241 (2002) 352-362

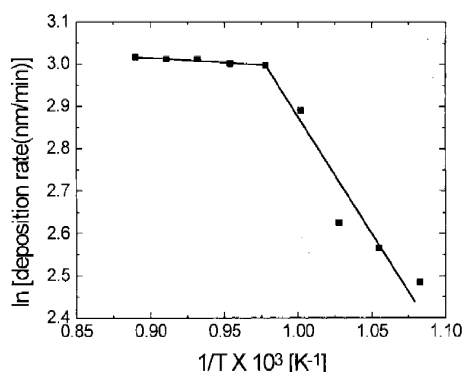


Fig 2. Arrhenius plot for the vapor phase deposition of a YSZ thin film on a {111} Si wafer using yttria and zirconia tetramethylheptanedionates.²

An example of the deposition behavior of YSZ films on a {111} Si wafer using yttria and zirconia tetramethylheptanedionates (thd), studied by Hwang and Shin⁴ is shown in Fig. 2, illustrating the two deposition regimes from surface reaction rate control at lower temperatures, or gas diffusion control at higher temperatures.

The progress of the deposition on micro-grooved substrates, which may serve as models for porous substrates, was studied by Akiyama et al¹, for the thd-MOCVD process.

The feedstock gas had a composition with $Y/(Y+Zr)=20\%$. The % numbers in Figure 3

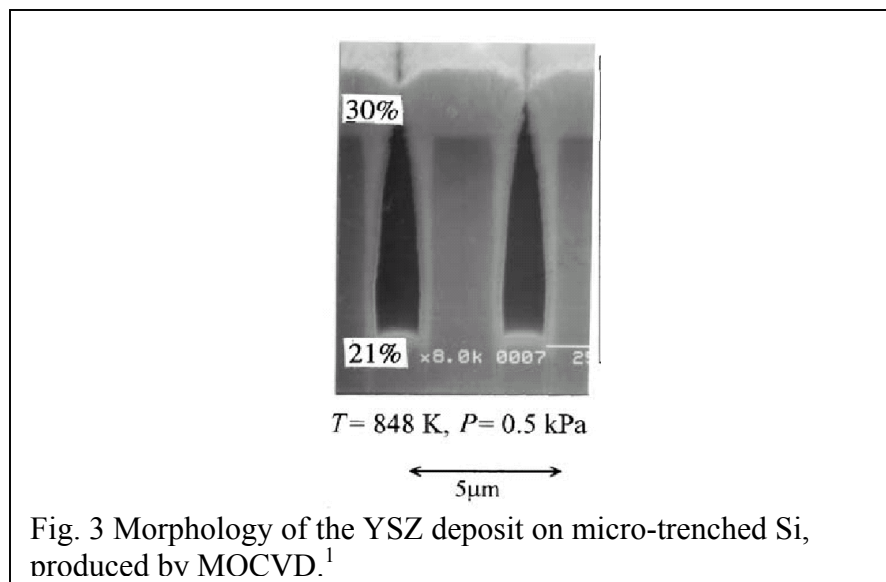


Fig. 3 Morphology of the YSZ deposit on micro-trenched Si, produced by MOCVD.¹

show that the $Y/(Y+Zr)$ can differ from the feed gas composition, for the indicated experimental temperature and pressure.

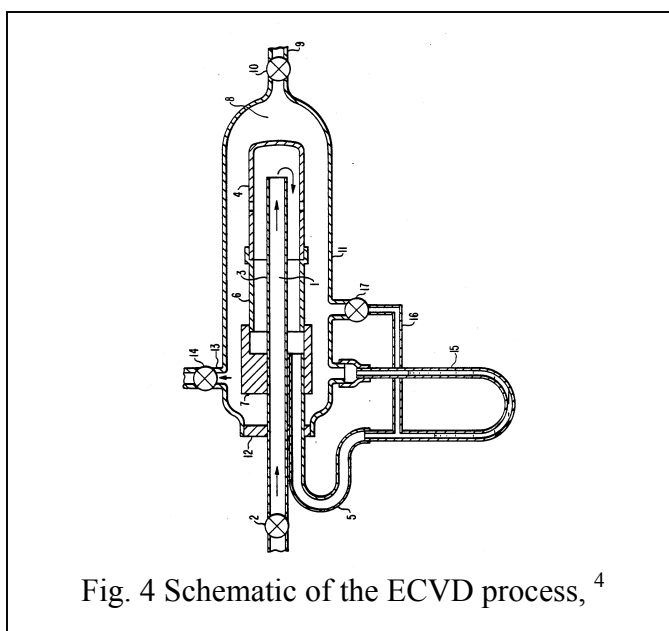
⁴ Sang-Chul Hwang and Hyung-Shik Shin, Effect of Deposition Temperature on the Growth of Yttria-Stabilized Zirconia Thin Films on Si(111) by Chemical Vapor Deposition *J. Am. Ceram. Soc.*, **82**, 2913 (1999)

Plasma enhanced MOCVD (PE-MOCVD) was used by Guiseppe and Selman⁵ to deposited YSZ on porous Ni-YSZ anode substrates, with substrate temperatures recommended in excess of 650 °C. The experiments illustrated the general difficulty of spanning large substrate pores (> 10 μm). Reduction of the substrate pore sizes to less than about 2 μm succeeded in covering if the pores by the deposited films.

The quality of the vapor deposited films generally can be improved by additional heating the assembly at higher temperatures ($T > 1000$ °C), but the introduction of additional processing steps would make it more difficult to meet the required cost goal.

Electrochemical and vapor-phase electrolytic deposition (ECVD and VED):

In these CVD –related methods electrolyte films can be formed on dimensionally invariant porous substrates. The method that has advanced most is the electrochemical vapor deposition, ECVD, on porous lanthanum strontium manganate cathodes.⁶ Mixtures of zirconium chloride and yttrium chloride vapors on one side of the porous cathode are reacted with an oxygen containing gas on the other side, as schematically shown in the original patent of Isenberg and Zymboly, Fig. 4. YSZ will deposit in the pores of the



⁵ Gianfranco Di Giuseppe and J. Robert Selman, Anode-supported planar solid oxide fuel cells by plasma-enhanced metalorganic chemical vapor deposition (PE-MOCVD) and electrostatic spray deposition (ESD): Fabrication of dense thin layers of yttria-stabilized zirconia by PE-MOCVD, *J. Mater. Res.*, **16**, 2983(2001)

substrates, eventually closing them off. After this stage, continued film growth is possible because of the finite electronic conductivity of the YSZ at the temperature of reaction. The rate formation of the film is then limited by the electronic conductivity of the YSZ, necessitating a relatively high processing temperature. Early ECVD experiments on alumina were discussed by Lin et al.⁷ Typical processing conditions for ECVD deposition on porous LSM cathodes, cited by Pal and Singhal⁸, were 1475K with a $P_{O_2}=10^{-4}$ atm, leading to a film thickness of about 50 μm in one hour. While electrolytes of excellent quality are produced, the process is fairly cost intensive. Variants of the process have been considered by Dollard et al.⁹, in which flaws in films formed by spray pyrolysis could possibly be healed by ECVD.

YSZ films deposited directly on dense and porous NiO, were examined by Inaba et al.¹⁰ In this case the NiO served as the oxygen source. The film formation rate at 1273K was found to be limited by oxygen transport in the pores of the NiO. After an initially fast formation of a film of about 1 μm film growth rates were about 2-3 μm in 5 hours. While this method offers the possibility of direct deposition on Ni-YSZ anodes, its growth rate limitation is unlikely to lead to a cost effective electrolyte film production.

An alternative method for YSZ electrolyte film formation was proposed by Uchimoto et al.¹¹. In this method, a conductive Ar glow discharge plasma is created in the reaction chamber by an RF generator. The plasma also contains zirconium and yttrium chloride vapor. The substrate is made cathodic versus a counter electrode and, at sufficient bias, YSZ is essentially electroplated on the substrate. Oxygen is obtained from $\text{H}_2\text{O}/\text{Ar}$ gas supplied to the back side of the cathode. On a porous conducting substrate such as LSM, the initial formation is by CVD, but once the pores are closed off, the YSZ deposition continues by direct electroplating. Since this method is not limited by the electronic conductivity of the YSZ, in principle, higher deposition rates could be expected than in the ECVD process. However, with the substrate held at 1173K, maximum growth rates of about 4 $\mu\text{m}/\text{hour}$ were obtained, about an order of magnitude slower than in the ECVD process. Part of the limitation of the VED process lies in the partial reduction of the deposited YSZ at the high biases necessary for rapid deposition. This partial reduction introduces electronic conductivity in the YSZ, leading to a corresponding decrease of the oxygen ion flux in the YSZ, and thus to a less efficient plating process.

⁶ A.O. Isenberg, in *Proc. ECS Symp. Electrode Materials, processes for Energy Conversion and Storage*, Vol-77-6, 1977, pg 963, J MacIntyre, S. Srinivasan and F. Will, Eds; and also, A. O. Isenberg and G. E. Zymboly, *U.S. Patent* 4,609,562, September 2, 1986.

⁷ Y.S. Lin, K.J. de Vries, H.W. Brinkman and A.J. Burggraaf, *Journal of Membrane Science*, **66**, 211 (1992).

⁸ U.Pal and S. Singhal, *J. Electrochem Soc.*, **137**, 2937(1990)

⁹ W. J. Dollard, G. R Folser; U. B. Pal, S. C. Singhal, *U. S. Patent* 5,085,742, February 4, 1992

¹⁰ Minoru Inaba, Atsushi Mineshige, Tomoyuki Maeda, Shinji Nakanishi, Tsutomu Ioroi, Tadayoshi Takahashi, Akimasa Tasaka, Kenji Kikuchi, Zempachi Ogumi, *Solid State Ionics* **104**, 303 (1997)

¹¹ Y. Uchimoto, K. Tsutsumi, T. Ioroi, Z. Ogumi, and Z.-I. Takehara, *J. Amer. Ceram. Soc.*, **83**, 77(2000).

Sol-gel methods

In sol-gel methods, an alkoxide with the general composition $M(OR)_n$, such as zirconium propoxide and yttrium propoxide, are deposited on the porous substrate electrode, and hydrolyzed under controlled conditions. The deposition is followed by a drying and firing step, possibly leading to a dense electrolyte film. Various aspects of stresses leading to damage of films due to strain mismatch¹² and in constrained sintering has been considered by several authors.¹³ In general, a critical thickness for supported films is found that depends mainly on the film fracture toughness and the film stress state. Further, film-substrate delamination or interface failure may also occur, if the effect of the film stress exceed the film-substrate interface strength.

An example of successful film formation by sol-gel methods on various substrates, including porous ones, was described by Kueper *et al*¹⁴, Fig. 5.

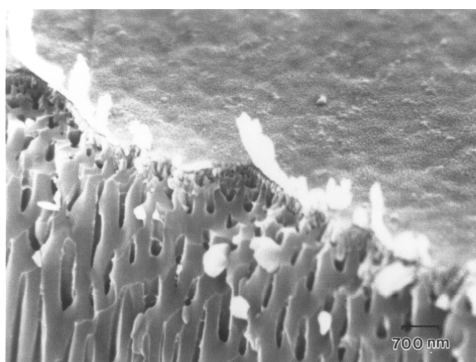


Fig. 5 YSZ thin film deposited by sol-gel methods on a porous alumina.¹⁴

Zirconium and yttrium isopropoxides were dissolved in methanol in a dry environment (e.g. glove box), with the addition of diethanolamine to promote solubility. Once removed from the dry environment, hydrolysis and condensation/polymerization occurs, increasing the viscosity of the solution. When an appropriate viscosity is reached, dip coating or spin coating leads to the formation of thin precursor film on the substrate. Rapid drying can actually improve the integrity of the film by limiting the polymerization and thus maintaining a more rubbery consistency of the dried film. For porous substrates making the surface non-wetting, such as by the deposition of sputtered gold film prior to the application of the sol-gel avoided the problem of the gel disappearing into the porous substrate. Slow heating during the drying process (less than 1°C/min) and subsequent sintering as low as 600°C could lead to the formation of a dense film on the porous

¹² M.D. Thouless, *J. Amer. Ceram. Soc.*, **73**, 2144(1990)

M.D. Thouless, E. Ollson, and A. Gupta, *acta metall. mater.*, **40**, 1287(1992)

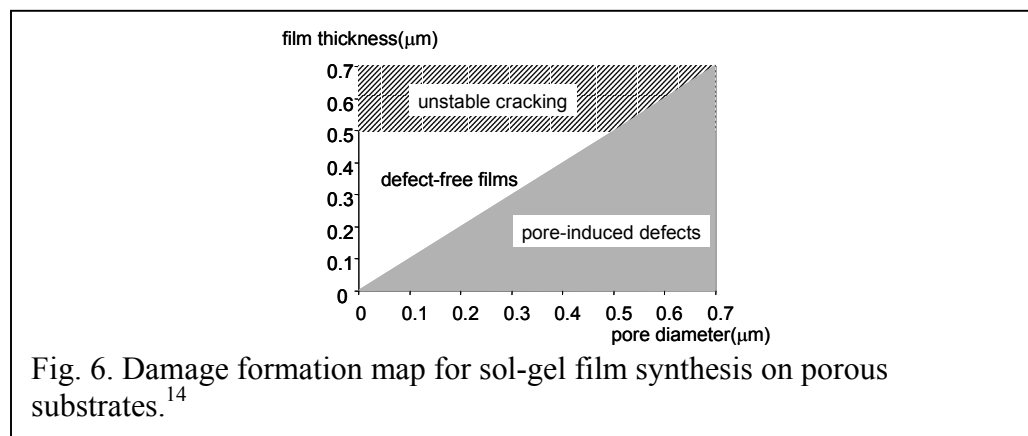
¹³ R.K. Bordia and A. Jagota, *J. Amer. Ceram. Soc.*, **76**, 2475 (1993)

M. Stech, P. Reynnders, and J. Rödel *J. Am. Ceram. Soc.*, **83**, 1889(2000)

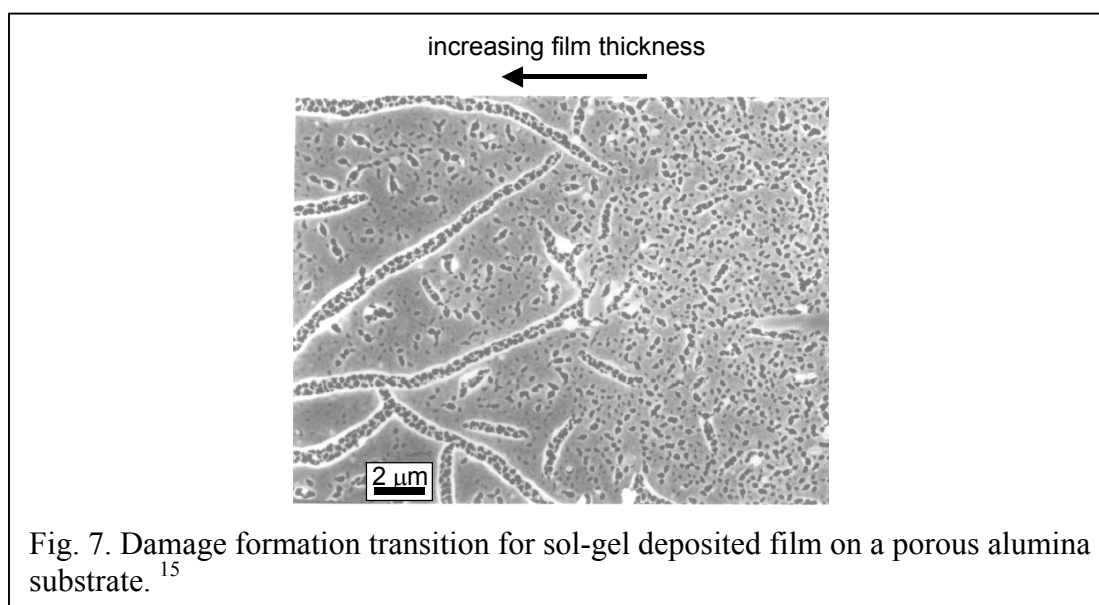
¹⁴ T.W. Kueper, S. J. Visco, and L. C. De Jonghe, *Solid State Ionics*, **52**, 251(1992)

substrate. Film thickness for one deposition is limited to a critical film thickness of at most 0.5 μm (more typically around 0.2 μm , however), above which unstable cracking will occur as a result of the film shrinkage during drying or densification. Thus, many repetitions of the deposition/densification process are required to achieve a film of the necessary thickness. The nature of the porous substrate is also critical in the sol gel processes. Large pores cannot be covered, leading to pore-induced defects thus requiring a substrate porosity that is both sub-micron and very uniform.

The general trends can be summarized in a graph, as shown in Fig. 6.



An example of a film transition thickness, with formation of pore-induced damage in the thin film region to onset of large unstable cracking is shown in Fig. 7.¹⁵

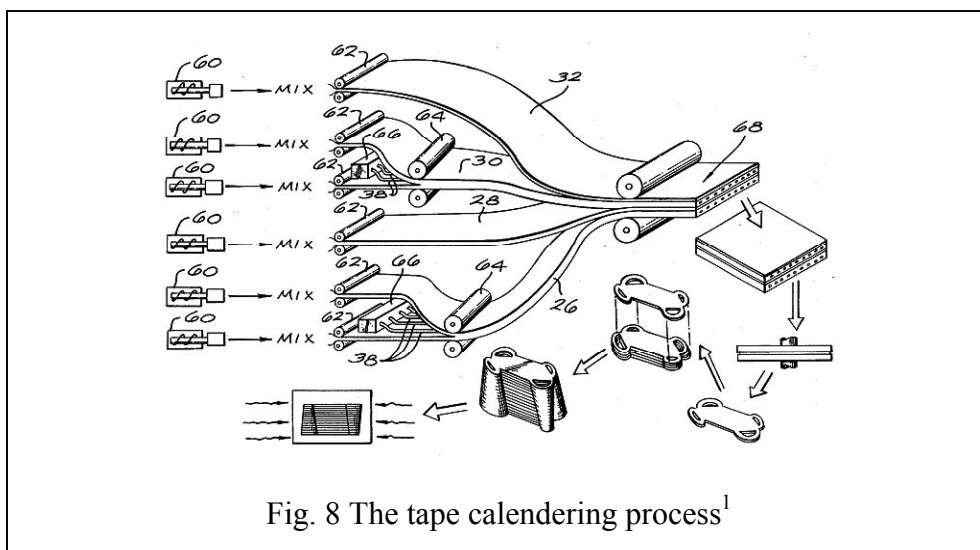


¹⁵ T.W. Kueper, "Sol-Gel derived ceramic electrolyte films on porous substrates," Ph.D. Thesis, U. California at Berkeley, May 1992; LBNL Report : LBL-32332 (1992)

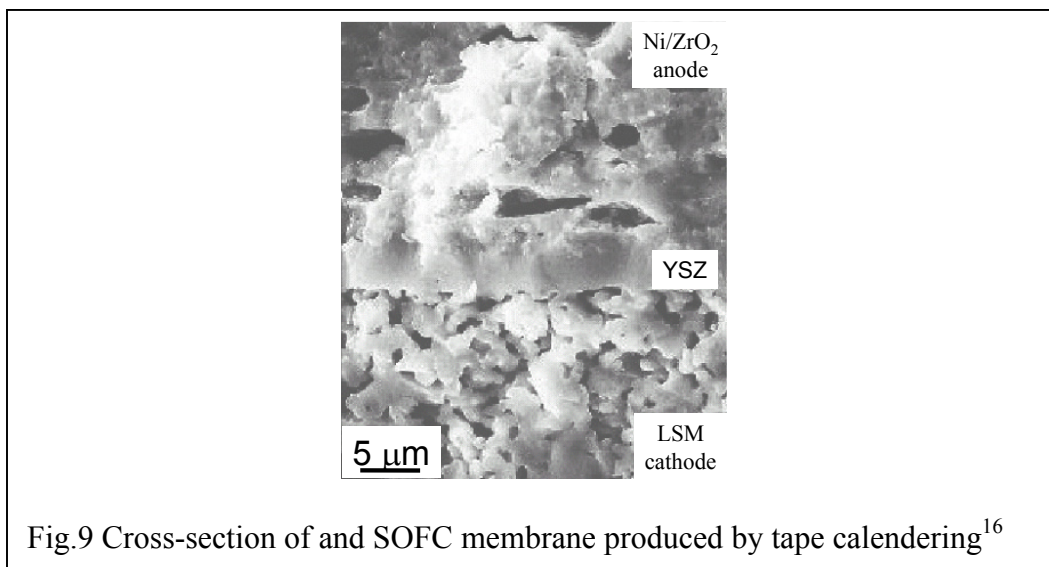
Powder Methods

Tape calendering

The tape calendering method¹⁶ is shown schematically in Fig. 8. The cell is constructed using multilayer tapes formed by first roll-milling several individual tapes (62) of cathode, electrolyte, anode, and interconnect material, and then roll-milling the multilayer tape to form a single membrane assembly (68). Gas channels are formed within the cathode and anode layers by incorporating organic fibers (38) into the tapes and burning out the fibers during the binder removal and sintering process.



An example of a membrane obtained by this methods shown in Fig. 9



¹⁶ D. Kotchick and N.Q. Minh, *Fabrication of a monolithic solid oxide fuel cell* U.S. Patent 4,913,982, April 3, 1990

Colloidal deposition

Electrophoretic deposition:

Electrophoretic deposition can be an effective way of depositing films onto porous substrates. The method involves the dispersion of colloidal particles in a carrier liquid, such as acetylacetone¹⁷ or alcohol, with an additional dispersant such as polyethyleneimine¹⁸. The basic aspects of electrophoretic deposition have been studied on various occasions, see *e.g.*¹⁹ Suspension stabilization and zeta potential control has also been achieved by dispersing zirconia powder in glacial acetic acid by Basu *et al.*²⁰ These authors reported a beneficial effect on the densification of the deposited film by using a fugitive carbon interlayer between the substrate and the deposit.

Typically, the suspensions are from quite dilute to up to 10 wt% of the powder, with deposition fields of a few 100 mV/cm. The porous, electronically conducting substrate which will become the fuel cell anode or cathode, is used as the cathode in the deposition process. Deposition rates depend on the suspension particle concentration and the applied voltages. Films of appropriate thickness can be deposited in a few minutes or less. The method is well suited for closed-end tubes²¹, while for flat plate geometries the back of the substrate may have to be protected from deposition.

Vacuum and capillary infiltration:

Vacuum infiltration is similar in many respects to the electrophoretic deposition on porous substrates. In this case, the deposit forms as a result of a vacuum produced *e.g.* by a mechanical pump, to the back of a porous substrate or inside a tube. Results are generally similar to those of electrophoretic deposition. Fine particles may, however, be pulled through the porous substrate in the early stages of deposition, and therefore, pore size and particle size should not differ too much.

Capillary infiltration is a simple method, similar to traditional slip casting, in which a particle suspension is put on a porous plaster mold²². A dilute dispersion of the YSZ, typically in alcohol, is simply painted or sprayed onto the porous substrate, and the

¹⁷ T. Ishihara, K. Shimose, T. Kudo, H. Nishiguchi, T. Akbay, and Y. Takita *J. Am. Ceram. Soc.*, **83**, 1921(2000).

¹⁸ J. Will, M. K. M. Hruschka, L. Gubler, and L. J. Gauckler *J. Am. Ceram. Soc.*, **84**, 328(2001)

¹⁹ D. De and Patrick S. Nicholson *J. Am. Ceram. Soc.*, **82**, 3031 (1999), and P. Sarkar and P. S. Nicholson, *J. Am. Ceram. Soc.*, **79**, 1987(1996).

²⁰ R. N. Basu, C. A. Randall, and M. J. Mayo, *J. Am. Ceram. Soc.*, **84**, 33(2001)

²¹ S. C. Singhal, "Advances in Solid Oxide Fuel Cell Technology," *Solid State Ionics*, **135**, 305 (2000).

²² M. N. Rahaman, "Ceramic Processing and Sintering," Marcel Dekker, Inc., New York, 1995, pp 299 ff.

solvent is removed by evaporation and by the capillary action of the substrate. This method was used successfully e.g. by Visco *et al.*²³ in the co-firing of a thin film fuel cell electrode and yttria-stabilized zirconia (YSZ). In this process, the YSZ powder particle size has to be well controlled and submicron, to allow for film densification below the temperatures where reactions between the YSZ and the electrode material can occur. The latter is particularly important when the supporting electrode is a lanthanum strontium manganate or related material for which resistive interfaces will form at temperatures above about 1380 °C. The success of the colloidal deposition and co-firing depends on the ability to develop a substrate structure that has a densification rate trajectory with temperature that is closely matched to that of the deposited film, to reduce film damage. Typically, the substrate has to be pre-fired to achieve this condition, and treatments leading to a matching of the densification rates of the film and the substrate follow after a series of dilatometry measurements. The rate matching is particularly important for flat plate geometries, where a minimum of warping is required. An example of a thin film SOFC cross section prepared by colloidal deposition and co-firing shown in Fig. 10.

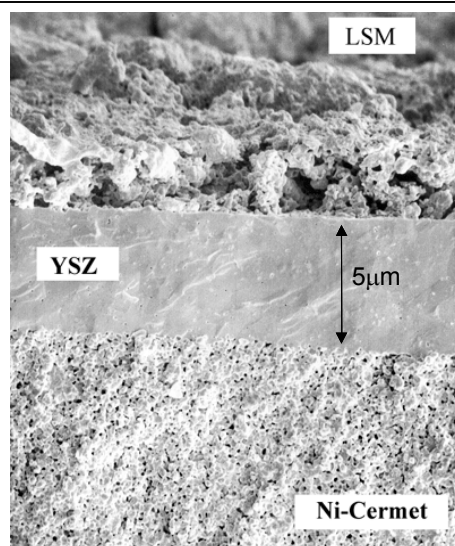


Fig. 10 Cross section of a thin film SOFC cross section prepared by colloidal deposition and co-firing.²³

Spray pyrolysis deposition:

In spray pyrolysis, a metallo-organic precursor such as a mixture of zirconium and yttrium acetylacetonates²⁴ or propoxides²⁵ is sprayed onto a heated substrate, kept

²³ S. J. Visco, C. Jacobson, and L. C. De Jonghe, "Fabrication and Performance of Thin-Film SOFCs"; in *Proceedings of the Fifth International Symposium on Solid Oxide Fuel Cells (SOFC-V)*. Edited by U. Stimming, S. C. Singhal, H. Tagawa, and W. Lehnert. The Electrochemical Society, Pennington, NJ, 1997.

²⁴ T. Setoguchi, M. Sawano, K. Eguchi and H. Arai, *Solid State Ionics*, **40-41**,502(1990)

at 400 -650°C. Various methods may be employed to produce droplets of appropriate size, with smaller droplets leading to better results. The droplets may be produced by a high velocity gas stream, by ultrasound dispersion, or by electrostatic means. Loss of powder due to overspraying can be a problem, which may be reduced by directing the droplets to the substrate by applying an electrostatic field. Film deposition rates of YSZ on porous electrodes were reported to be as high as 60 $\mu\text{m/hr}$ by Choy et al.²⁶

Summary

Various processing methods for producing supported thin film electrolytes for solid oxide fuel cells have been described. The cost issue is an important constraint. The most cost effective ones are likely to be simple powder methods combined with co-firing.

Acknowledgement

This work was supported by the U.S. Department of Energy, National Energy Technology Laboratory.

²⁵ H. Ruiz, H. Vesteghem, and A.R. Di Giampaolo, and J. Lire, *Surface Coatings Technology*, **89**, 77(1997)

²⁶ K.L. Choy, in: W.E. Lee (Ed.), *British Ceramic Proc.*, **54**, 1995, p. 65.